Synthesis and application of novel ionic phosphine ligands with a cobaltocenium backbone

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Abstract

Six novel ionic phosphine ligands with a cobaltocenium backbone, 1,1′-bis(dicyclohexylphosphino) cobaltocenium hexafluorophosphate (di-cypc$^+$PF$_6^-$) (**1a**), 1,1′-bis(di-*iso*-propylphosphino) cobaltocenium hexafluorophosphate (di-isoppc$^+$PF$_6^-$) (**2a**), 1,1′-bis(di-*tert*-butylphosphino) cobaltocenium hexafluorophosphate (di-tbpc$^+$PF$_6^-$) (**3a**), and the monophosphine ligand Cc$^+$PR$_2$PF$_6^-$ (Cc$^+$ = cobaltocenium; R = Cy, **1b**; R = *i*-Pr, **2b**; R = *t*-Bu, **3b**) were synthesized and characterized by elemental analysis, spectroscopy, and X-ray diffraction techniques. These ligands are air-stable and useful for Suzuki coupling reactions in the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIM$^+$PF$_6^-$), enabling high catalytic activity.
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Keywords: Ionic phosphine ligands; Cobaltocenium; Synthesis; Suzuki coupling reactions; Ionic liquids

1. Introduction

Metallocene derivatives have found widespread use as ligands. In particular, phosphine ligands based on substituted ferrocenes have been widely used [1]. Phosphine ligands based on substituted cobaltocenium are difficult to be synthesized in large scale, and only 1,1′-bis(diphenylphosphino) cobaltocenium hexafluorophosphate (dppc$^+$PF$_6^-$) has been used in catalytic hydroformylation [2]. Compared with the isoelectronic ferrocenes, cobaltocenium cations show different reactivity on the cyclopentadienyl rings due to their electron-withdrawing properties. Owing to their ionic character, they show good solubility in polar solvents and ionic liquids. These properties stimulated our interest in synthesizing novel cobaltoceniumyl-phosphines and in testing them as ligands in Suzuki coupling reactions in ionic liquids.

The palladium-catalyzed Suzuki coupling reaction is one of the most efficient methods for the construction of C–C bonds and has found widespread use in organic synthesis [3]. However, the separation of the products from the reaction mixture, the recovery of the catalysts, and the need for organic solvents are the major disadvantages in the Suzuki cross-coupling reactions. For these reasons, many Suzuki coupling reactions are not used on an industrial scale despite their benefits. To overcome these problems, some heterogeneous Pd-catalyzed Suzuki coupling systems have been introduced, such as the use of aqueous media [4] and ionic liquids [3b,5]. The use of ionic liquids as solvents for the Suzuki coupling reactions is a very attractive approach [5,6]. The products can be separated from ionic liquids by extraction with organic solvents and the catalytic solution can be reused. Generally, neutral phosphine ligands are used to complex the palladium species, resulting in excellent results for the palladium-catalyzed Suzuki coupling reactions [5a]. However, the separation of the products with neutral phosphine ligands and Pd-catalyst is difficult because neutral phosphine ligands and catalyst easily dissolve in organic solvents. To overcome these problems, a new catalyst system consisted of PdCl$_2$/ionic phosphine ligand/ionic liquid was suggested.

In the present article, we describe the synthesis and characterization of six novel ionic phosphine ligands with a cobaltocenium backbone and their successful applications in Suzuki coupling reactions using ionic liquids as solvent.

2. Results and discussion

2.1. Synthesis and characterization of ionic phosphine ligand

We synthesized 1,1′-bis(di-cyclohexylphosphino) cobaltocenium hexafluorophosphate (di-cypc$^+$PF$_6^-$, **1a**) following the method given by Wasserscheid [2]. The substituted cyclopentadiene C$_5$H$_5$PCy$_2$ was obtained from NaCp; subsequent deprotonation with n-BuLi generated the anionic ligand, and in situ reaction with CoCl$_2$ afforded bidentate cobaltocenylphosphine. Oxidation of this cobaltocenylphosphine to the ionic phosphine is difficult because the phosphine can also be easily oxidized to phosphine oxide [7]. Using the smooth anaerobic oxidation method, we were able to obtain **1a** in high yield free of phosphine oxides. The cobaltocenylphosphine reacted with C$_2$Cl$_6$ to generate the green 1,1′-bis(di-cyclohexylphosphino)cobaltocenium chloride, and anion exchange with NH$_4$PF$_6$ led to air-stable yellow solid **1a**. Besides the bidentate phosphine ligand, a small amounts of monophosphine Cc$^+$P(Cy)$_2$PF$_6^-$ **1b** (Cc$^+$ = cobaltocenium) was also obtained.

Using this procedure, we were able to obtain **2a** 1,1′-bis(di-iso-propylphosphino) cobaltocenium hexafluorophosphate (di-isoppc$^+$PF$_6^-$) and **3a** 1,1′-bis(di-tert-butylylphosphino) cobaltocenium hexafluorophosphate (di-tbpc$^+$PF$_6^-$), together with small amounts of **2b** (Cc$^+$P-(i-Pr)$_2$PF$_6^-$) and **3b** (Cc$^+$P(t-Bu)$_2$PF$_6^-$), respectively (see Scheme 1).

These ionic ligands were fully characterized by elemental analysis, ^{1}H NMR, ^{31}P NMR and X-ray diffraction analysis. The ^{1}H NMR spectra of **1a**, **2a** and **3a** show two singlets at 5.81 and 5.97 ppm, 5.49 and 5.76 ppm, 5.67 and 5.89 ppm, respectively, for their H^3/H^4 and H^2/H^5 protons of the substituted Cp rings.

Crystals of these ligands were obtained by slow diffusion of hexane into acetone solutions of the ligands. The molecular structures of **1a**, **2a**, **3a**, **1b**, **2b** are shown in Figs. 1–5, respectively (for the information of **3b**, see Ref. [8]). As can be seen in Figs. 1–3, the structures of the three bidentate ligands are very similar to each other. For example, (I) the two substitute Cp rings are not parallel with a dihedral
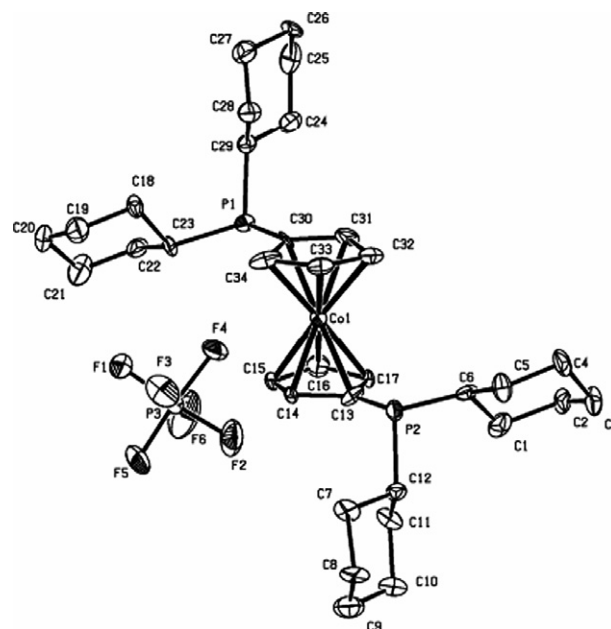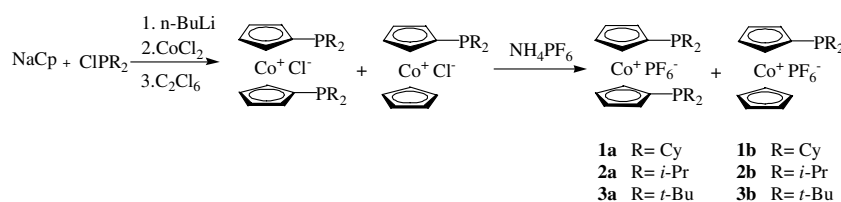

Fig. 1. ORTEP diagram of **1a**. Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (°): Co(1)–C(13) = 2.058(12), C(13)–P(2) = 1.850(14), C(12)–P(2) = 1.908(14), C(23)–P(1) = 1.877(13), C(30)–P(1) = 1.819(13); C(30)–P(1)–C(29) = 102.8(5), C(30)–P(1)–C(23) = 105.0(6).

angle of 8.1(7)° for **1a**, 1.1(2)° for **2a**, and 4.8(2)° for **3a**, (II) the average distance between the Co atom and the center of Cp ring is 1.6573 Å for **1a**, 1.6430 Å for **2a**, and 1.6445 Å for **3a**, (III) the two R$_2$P substituents in the cation {[η^5-R$_2$PC$_5$H$_4$]$_2$Co}$^+$ of **1a**, **2a** or **3a** are trans to each other with respect to the Co metal center.

2.2. Catalysis in ionic liquid

The catalytic systems were prepared in situ by mixing PdCl$_2$ with the ligand in BMIM$^+$PF$_6^-$. The results obtained in Suzuki coupling reaction of phenyl bromide with phenyl boronic acid using different ligands are summarized in Table 2. We found that the six ligands are stable in air and active for the Suzuki coupling reaction. The trend in the catalytic activity of the bidentate ligands for Suzuki coupling reaction is **1a** < **2a** < **3a**; The catalytic activity of monophosphine ligands has a similar trend (**1b** < **2b** < **3b**). This is in good accordance with reported results for Cp$_2$Fe(PR$_2$)$_2$ [9].

NaCp + ClPR$_2$ $\xrightarrow[\text{3.C}_2\text{Cl}_6]{\substack{\text{1. n-BuLi}\\ \text{2.CoCl}_2}}$

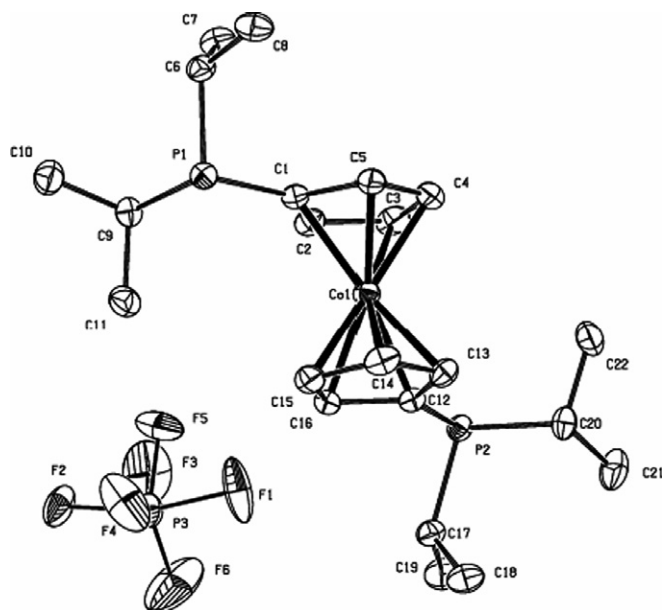|	
1a R= Cy	**1b** R= Cy
2a R= i-Pr	**2b** R= i-Pr
3a R= t-Bu	**3b** R= t-Bu

Scheme 1.

Fig. 2. ORTEP diagram of **2a**. Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (°): Co(1)–C(1) = 2.063(3), C(1)–P(1) = 1.832(3), C(6)–P(1) = 1.868(3), C(12)–P(2) = 1.834(3), C(17)–P(2) = 1.872(3); C(1)–P(1)–C(9) = 102.67(13), C(1)–P(1)–C(6) = 97.92(13).
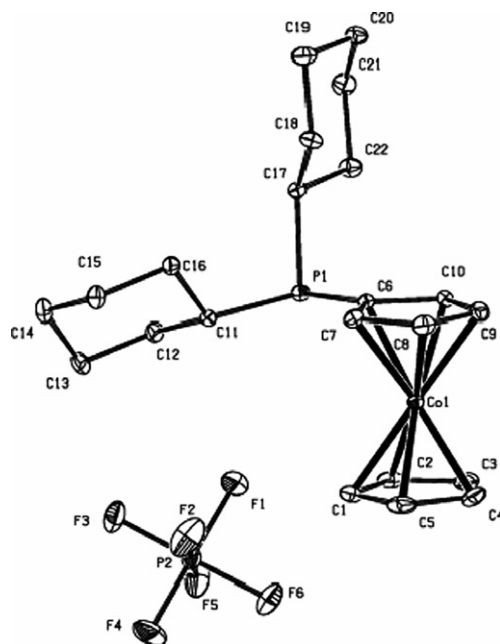

Fig. 4. ORTEP diagram of **1b**. Thermal ellipsoid are shown at the 50% level. Selected bond lengths (Å) and angles (°): Co(1)–C(1) = 2.032(5), C(6)–P(1) = 1.833(4), C(11)–P(1) = 1.842(4), C(17)–P(1) = 1.864(4), C(6)–P(1)–C(11) = 103.70(17), C(6)–P(1)–C(17) = 101.88(17).
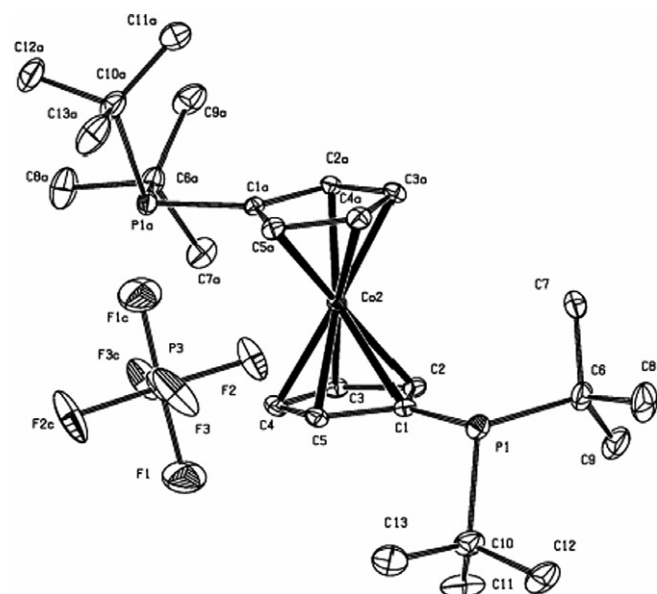

Fig. 3. ORTEP diagram of **3a**. Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (°): Co(2)–C(1) = 2.074(3), C(1)–P(1) = 1.837(3), C(6)–P(1) = 1.882(4), C(10)–P(1) = 1.900(5), C(1a)–P(1a) = 1.890(5), C(6a)–P(1a) = 1.829(3), C(1)–P(1)–C(6) = 105.79(17), C(6)–P(1)–C(10) = 110.2(2).
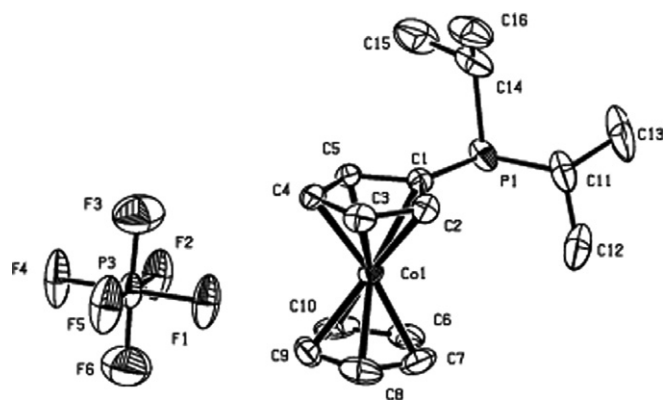

Fig. 5. ORTEP diagram of **2b**. Thermal ellipsoid are shown at the 50% level. Selected bond lengths (Å) and angles (°): Co(1)–C(1) = 2.060(4), C(14)–P(1) = 1.851(6), C(11)–P(1) = 1.847(6), C(1)–P(1) = 1.816(5), C(1)–P(1)–C(11) = 101.8(2), C(1)–P(1)–C(14) = 99.2(3).

Coupling of phenyl boronic acid with a variety of aryl bromides was conducted using three bidentate ligands as illustrated in Table 3. Our first model, bromobenzene, gave an excellent result of a 98% conversion of starting aryl bromide and an isolated purified product yield of 92%, utilizing 1.0 mol% catalyst (entry 1). Then we tested the scope of the reaction with a range of substituted aryl bromides with varying electronic properties. The aryl bromides with electron-donating groups, such as methyl (entries 2–4) and methoxy (entries 5–7), gave excellent yields, while aryl bromide with electron-withdrawing groups, such as nitro, trifluoromethyl and acetyl, gave the coupling products almost quantitatively. The trend in the reactivity is expected for Suzuki coupling. It was noteworthy that 2-bromothiophene also gave the desired product in an excellent yield with this catalytic system (entry 17). In contrast Colacot found that bromothiophene is a difficult substrate to couple when neutral phosphine-based catalysts were employed [9]. Additionally, a

Table 1
Selected crystal data, data collection, and structure refinements for compounds **1a**–**3a**, **1b**, and **2b**

	1a	2a	3a	1b	2b
Formula	$C_{34}H_{44}CoF_6P_3$	$C_{22}H_{36}CoF_6P_3$	$C_{26}H_{44}CoF_6P_3$	$C_{22}H_{31}CoF_6P_2$	$C_{16}H_{23}CoF_6P_2$
Formula weight	718.53	566.35	622.45	530.34	450.21
Temperature (K)	293(2)	293(2)	293(2)	292(2)	292(2)
Crystal color	Yellow	Yellow	Yellow	Yellow	Yellow
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P1$	$P2(1)/c$	$P2/c$	$P\bar{1}$	$P2(1)/c$
a (Å)	6.4358(6)	8.0389(4)	11.7428(11)	6.4097(8)	19.9996(19)
b (Å)	9.4851(8)	22.6962(12)	10.0264(10)	9.4244(12)	14.9998(15)
c (Å)	14.3753(13)	14.7397(8)	26.965(3)	19.695(2)	14.4927(14)
α (°)	94.8580(10)	90	90	81.078(2)	90
β (°)	97.176(2)	97.9670(10)	92.670(2)	82.544(2)	110.038(2)
γ (°)	99.3430(10)	90	90	81.751(2)	90
V (Å^3)	854.15(13)	2663.3(2)	3171.3(5)	1156.1(2)	4084.5(7)
Z	1	4	2	2	8
D_c (mg m^{-3})	1.397	1.412	1.304	1.523	1.464
Absolute coefficient (mm^{-1})	0.699	0.875	0.741	0.936	1.045
$F(000)$	374	1176	1304	548	1840
θ Range	2.87–28.24°	1.66–28.26°	1.74–25.00°	2.11–26.00°	1.74–25.99°
	3157	16,895	15,577	9275	32,212
Number of reflections	2717	5271	5581	4465	7987
Number of independent reflections	0.0325	0.0482	0.0286	0.0828	0.1027
R(int)	0.988	0.805	1.094	0.996	0.959
Goodness-of-fit on F^2	$R_1 = 0.0482$	$R_1 = 0.0442$	$R_1 = 0.0565$	R1 = 0.0653	$R_1 = 0.0613$
Final R indices	$wR_2 = 0.1188$	$wR_2 = 0.0944$	$wR_2 = 0.1412$	$wR_2 = 0.1585$	$wR_2 = 0.1706$
	$R_1 = 0.0588$	$R_1 = 0.0781$	$R_1 = 0.0683$	$R_1 = 0.0863$	$R_1 = 0.0937$
$[I > 2\sigma(I)]$	$wR_2 = 0.1243$	$wR_2 = 0.1013$	$wR_2 = 0.1487$	$wR_2 = 0.1690$	$wR_2 = 0.1955$
R indices (all data) largest difference in peak and hole (e Å^{-3})	0.477, −0.196	0.265, −0.194	0.434 , −0.275	1.234, −0.311	0.587, −0.640

challenging problem in Suzuki coupling processes is the ability to combine sterically hindered substrates. It is particularly difficult when coupling partners have large *ortho* substituents. We found that it was efficient to couple the sterically hindered 2-bromomesitylene with aryl boronic acid (entry 18). The above procedure is not efficient for the coupling of aryl chloride and aryl boronic acid, even using **3a**/PdCl$_2$ as the catalyst, only 30% biphenyl product was detected upon heating at 120 °C for 3 h, while Cp$_2$Fe(PR$_2$)$_2$PdCl$_2$ (R = i-Pr, t-Bu) was shown to be an efficient catalyst for aryl chlorides [9,10]. Considering the structural similarity of both kinds of ligands, their different influence on the reaction activity has to be attributed to electronic reasons. The electron density at the phospho-

rus atoms is significantly lower in the case of ionic ligand due to the electron-withdrawing effect of the formal cobalt(III) central atom in the ligand. This interpretation is supported by former work [2].

The reusability of the present catalyst system was examined in the coupling reaction of bromobenzene with aryl boronic acid. Unfortunately, the catalyst system can only be reused 2–3 times (Table 4).

3. Conclusion

We describe the synthesis and characterization of six novel ionic phosphine ligands with a cobaltocenium backbone by Wasserscheid's method. These ionic phosphine

Table 2
Relative reactivities of ligand/PdCl$_2$ for the coupling of bromobenzene and phenyl boronic acid in BMIM PF$_6$

Entry	Ligand	Temperature (°C)	Time (h)	Yield[a] (%)
1	**1a**	110	0.5	98
2	**1b**	100	0.5	99
3	**2a**	90	0.5	98
4	**2b**	80	0.5	98
5	**3a**	70	0.5	99
6	**3b**	60	0.5	98
7	–	110	0.5	81
8	–	60	0.5	35
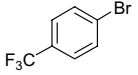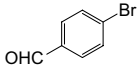
[a] GC yield using hexadecane as internal standard.

Table 3
Suzuki cross-coupling reaction of halobenzens with phenylbronic acid catalyzed by ligand/PdCl$_2$ in BMIM PF$_6$
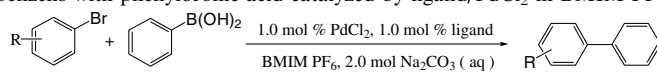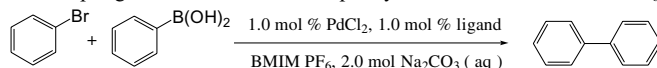
Entry	Substrate	Ligand	Temperature (°C)	Time (h)	Yield[a,b] (%)
1		**1a**	110	0.5	98(92)
		2a	80	0.5	98(93)
		3a	60	0.5	98(92)
2		**1a**	100	0.5	95(87)
		2a	80	1	99(94)
		3a	60	1.5	94(85)
3		**1a**	100	0.5	98(94)
		2a	80	1	98(92)
		3a	60	1.5	98(90)
4		**1a**	100	0.5	98(92)
		2a	80	1	98(92)
		3a	60	2	93(85)
5		**1a**	100	2	98(92)
		2a	80	2	90(84)
		3a	60	1.5	94(85)
6		**1a**	100	1	98(90)
		2a	80	1.5	95(88)
		3a	60	1.5	95(86)
7		**1a**	100	2	97(91)
		2a	80	1.5	92(86)
		3a	60	1.5	90(87)
8		**1a**	100	0.5	99(92)
		2a	80	1	95(90)
		3a	60	1	92(86)
9		**1a**	100	0.5	99(93)
		2a	80	1	96(90)
		3a	60	1	95(88)
10		**1a**	100	0.25	99(92)
		2a	80	0.5	98(92)
		3a	60	0.5	94(85)
11		**1a**	100	0.25	99(92)
		2a	80	0.5	96(91)
		3a	60	0.5	96(89)

Table 3 (*continued*)

Entry	Substrate	Ligand	Temperature (°C)	Time (h)	Yield[a,b] (%)
12		**1a**	100	0.25	98(91)
		2a	80	1.5	98(92)
		3a	60	0.5	98(90)
13		**1a**	100	0.25	95(90)
		2a	80	1.5	95(90)
		3a	60	0.5	95(91)
14		**1a**	100	0.25	99(92)
		2a	80	1	95(92)
		3a	60	0.5	95(90)
15		**1a**	100	0.25	99(92)
		2a	80	1	96(91)
		3a	60	0.5	97(91)
16		**1a**	100	0.25	99(93)
		2a	80	1	98(92)
		3a	60	0.5	99(92)
17		**1a**	100	0.25	99(94)
		2a	80	0.5	93(88)
		3a	60	0.5	95(90)
18		**1a**	100	2	91(84)
		2a	80	3	95(86)
		3a	60	2	95(83)

[a] GC yield using hexadecane as internal standard.
[b] Isolate yields are given in parentheses.

Table 4
Relative reactivities of ligand/PdCl$_2$ for the coupling of bromobenzene and phenyl boronic acid in BMIM PF$_6$

$$\text{PhBr} + \text{PhB(OH)}_2 \xrightarrow[\text{BMIM PF}_6,\ 2.0\ \text{mol Na}_2\text{CO}_3\ (\text{aq})]{1.0\ \text{mol \% PdCl}_2,\ 1.0\ \text{mol \% ligand}} \text{Ph-Ph}$$

Run	Ligand		
	1a (%)	**2a** (%)	**3a** (%)
1	98[a]	99[a]	98[a]
2	92[a]	95[a]	95[a]
3	60[a]	45[a]	20[a]

[a] GC yield using hexadecane as internal standard.

ligands/PdCl$_2$ are air-stable catalysts for aryl bromide Suzuki coupling reactions. The trend in the reactivity of these catalysts is **1a**/PdCl$_2$ < **2a**/PdCl$_2$ < **3a**/PdCl$_2$, **1b**/PdCl$_2$ < **2b**/PdCl$_2$ < **3b**/PdCl$_2$. The increase in activity is attributed to the increase in electron density of the phosphine ligand. Work is in progress in demonstrating the activities and reusablities of these catalysts in Sonogashira, Heck and Negishi coupling reactions.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of highly purified nitrogen using standard Schlenk or vacuum-line techniques. THF was distilled under nitrogen from sodium/benzophenone ketyl. All solvents were

bubbled for at least 15 min before use. Elemental analyses were performed on an Elementar Vario El analyzer. ^{1}H NMR and ^{31}P NMR spectra were obtained on a Varian MERCURY Plus 400 MHz spectromer. ^{1}H NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

4.2. Preparation of 1,1'-bis(dicyclohexylphosphino) cobaltocenium hexafluorophosphate (1a) and (di-cyclohexylphosphino)cobaltocenium hexafluorophosphate (1b)

To the freshly prepared NaCp (21 mmol) in THF, ClPCy$_2$ (21 mmol) dissolved in ether was added at −30 °C. The reaction mixture was stirred for 1.5 h at room temperature, then cooled to −78 °C. n-BuLi (2.5 M in hexane, 21 mmol) was added dropwise. The mixture was stirred for 1.5 h at room temperature. CoCl$_2$ (10.5 mmol) was added, producing a dark brown solution. After stirring this solution overnight under reflux, C$_2$Cl$_6$ (13 mmol) was added. The resulting solution was stirred at room temperature for another 10 min. After evaporation of all volatile substances in vacuo, the residue was dissolved in 100 mL of CH$_2$Cl$_2$ and filtered through Celite to remove LiCl. The filtrate was dried in vacuo to obtain an oily, brown residue. The oil was dissolved in 150 mL of CH$_2$Cl$_2$, NH$_4$PF$_6$ (11 mmol) in water was added and stirred for 1 h, no precipitate was formed. The solution was added to 150 mL of water, and extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic layers were dried over MgSO$_4$, and filtered. After evaporation of solvent in vacuo, the residue was subject to column chromatography (silica gel, CH$_2$Cl$_2$) to give a yellow solid 1a (yield: 51%) and a yellow solid 1b (yield: 14%).

Compound 1a: Anal. Calc. for C$_{34}$H$_{52}$CoF$_6$P$_3$: C, 56.20; H, 7.21. Found: C, 56.15; H, 7.18%. ^{1}H NMR (CDCl$_3$): δ 1.13–1.96 (m, 44H, 4Cy): 5.81 (s, 4H, C$_5$H$_2$H$_2$), 5.97 (s, 4H, C$_5$H$_2$H$_2$) ppm. ^{31}P NMR (CDCl$_3$): δ −9.93 (s), −144.05 (quintet, $J_{P–F}$ = 711 Hz) ppm.

Compound 1b: Anal. Calc. for C$_{22}$H$_{31}$CoF$_6$P$_2$: C, 49.82; H, 5.89. Found: C, 49.76; H, 5.83%. ^{1}H NMR (CDCl$_3$): δ 1.03–1.88 (m, 22H, 2Cy): 5.65 (s, 5H, C$_5$H$_5$), 5.67 (s, 2H, C$_5$H$_2$H$_2$), 5.98 (s, 2H, C$_5$H$_2$H$_2$) ppm. ^{31}P NMR (CDCl$_3$): δ −9.33(s), −144.50 (quintet, $J_{P–F}$ = 711 Hz) ppm.

4.3. Preparation of 1,1'-bis(di-iso-propylphosphino) cobaltocenium hexafluorophosphate (2a) and (di-iso-propylphosphino)cobaltocenium hexafluorophosphate (2b)

Compound 2a and 2b were prepared similarly, with ClP(i-Pr)$_2$ instead of ClPCy$_2$, in 59% (2a) and 12% yields (2b).

Compound 2a: Anal. Calc. for C$_{22}$H$_{36}$CoF$_6$P$_3$: C, 46.65; H, 6.41. Found: C, 46.60; H, 6.38%. ^{1}H NMR (CDCl$_3$): δ 1.07 (m, 24H, 8CH$_3$), 2.05 (m, 4H, CH), 5.49 (s, 4H, C$_5$H$_2$H$_2$), 5.76 (s, 4H, C$_5$H$_2$H$_2$) ppm. ^{31}P NMR (CDCl$_3$): δ −3.03(s), −145.92 (quintet, $J_{P–F}$ = 711 Hz) ppm.

Compound 2b: Anal. Calc. for C$_{16}$H$_{23}$CoF$_6$P$_2$: C, 42.68; H, 5.15. Found: C, 42.55; H, 5.26%. ^{1}H NMR (CDCl$_3$): δ 1.10 (m, 12H, 4CH$_3$), 2.06 (m, 2H, CH), 5.70 (s, 5H, C$_5$H$_5$), 5.71 (s, 2H, C$_5$H$_2$H$_2$), 5.98 (s, 2H, C$_5$H$_2$H$_2$) ppm. ^{31}P NMR (CDCl$_3$): δ −2.26 (s), −145.67 (quintet, $J_{P–F}$ = 711 Hz) ppm.

4.4. Preparation of 1,1'-bis(di-tert-butylphosphino) cobaltocenium hexafluorophosphate (3a) and (di-tert-butylphosphino)cobaltocenium hexafluorophosphate (3b)

Compound 3a and 3b were prepared similarly, with ClP (t-Bu)$_2$ instead of ClPCy$_2$, in 12% (3a) and 8% yields (3b).

Compound 3a, Anal. Calc. for C$_{26}$H$_{44}$CoF$_6$P$_3$: C, 50.17; H, 7.12. Found: C, 50.54; H, 7.11%. ^{1}H NMR (CDCl$_3$): δ 1.24 (s, 18H, 6CH$_3$), 1.27 (s, 18H, 6CH$_3$), 5.67 (s, 4H, C$_5$H$_2$H$_2$), 5.89 (s, 4H, C$_5$H$_2$H$_2$) ppm. ^{31}P NMR (CDCl$_3$): δ 23.25 (s), −145.90 (quintet, $J_{P–F}$ = 711 Hz) ppm.

Compound 3b: Anal. Calc. for C$_{18}$H$_{27}$CoF$_6$P$_2$: C, 45.20: H, 5.69. Found: C, 45.15; H, 5.32%. ^{1}H NMR (CDCl$_3$): δ1.24 (s, 9H, 3CH$_3$), 1.26 (s, 9H, 3CH$_3$), 5.71 (s, 5H, C$_5$H$_5$), 5.78 (s, 2H, C$_5$H$_2$H$_2$), 6.04 (s, 2H, C$_5$H$_2$H$_2$) ppm. ^{31}P NMR (CDCl$_3$): δ 24.32 (s), −145.88 (quintet, $J_{P–F}$ = 711 Hz) ppm.

4.5. X-ray crystal structure analysis

Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of 1a in acetone at room temperature. The crystals of 2a, 3a, 1b, 2b were obtained by the similar method. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD 4K diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed using SAINT version 6.45 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.14 software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Further crystallographic details were summarized in Table 1.

4.6. Catalytic experiments in ionic liquid

In a typical experiment (Table 2, entry 1), a 25 mL round-bottom flask, equipped with a magnetic bar and a condenser, was charged with PdCl$_2$(0.0025 mmol), ligand 1a (0.0025 mmol) and BMIM$^+$PF$_6^-$(5 mL). The mixture was stirred at 110 °C until a dark brown mixture was obtained (at least 1 h); phenyl bromide (0.25 mmol), phenyl boronic acid (0.375 mmol), and a solution of Na$_2$CO$_3$ (0.5 mmol) in water were added. The mixture was heated with vigorous stirring until the peak of phenyl bromide on GC disappeared, then cooled and extracted with diethyl

ether; the combined extracts were washed by brine, water and dried. After removal of the solvent in vacuo, the mixture was chromatographed on a silica pad to afford the diaryl products in high purity as characterized by GC–MS, ^{1}H NMR spectroscopy.

4.7. Procedure for the catalyst recycling of Suzuki coupling reaction

After completion of the reaction and cooling to room temperature, the products and the unreacted reagents were extracted with diethyl ether, then washed with water and dried in vacuum. The resulting viscous $PdCl_2$/ligand/ $BMIM^+PF_6^-$ mixture was charged with fresh reagents (aryl halide, phenyl boronic acid and the solution of Na_2CO_3 in water) and heated at the required temperature with stirring for the proper time.

5. Supplementary data

CCDC 640044, 640045, 640046, 640047 and 640048 contain the supplementary crystallographic data for **1a**, **2a**, **3a**, **1b** and **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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